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<b>6. AUTHOR(S)</b> Jaroslav Vacek			
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Department of Complex molecular Systems J. Heyrovsky Institute of Physical Chemistry Dolejskova 3, Prague 8, 18223, Czech Republic		<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  4	
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**13. ABSTRACT (Maximum 200 Words)**

We calculated the friction coefficients and their dependence on rotation frequency in carborane rotors and propellers. A paper on this is almost ready for submission. A copy of the draft is attached. Our results indicate that molecular rotors can be used to control friction of surfaces to some extent. Further investigation is needed.

A new phenomenological model of molecular propeller action was designed. Its performance is currently being tested also for porphyrin types of rotors.

We designed a new generation of our light-absorption driven molecular motor.

**14. SUBJECT TERMS**

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## Molecular Tinkertoy Construction Kit: Computer Simulations of Molecular Propellers and Paddle Wheels

### Introduction

We used molecular dynamics (MD) simulation techniques and universal force field (UFF) implemented in our computer program TINK<sup>1</sup> to study friction in molecular-sized rotors, propellers and motors. We finished evaluation of friction in carborane based molecular propellers (1), designed a simple model to describe molecular propeller response to gas flow (2), designed a new generation of the light-absorption driven motor<sup>2</sup> (3) and performed *ab initio* calculations of rotation barriers in simple bromobenzene rotors.

### Statement of Work

#### *(1) Friction in the carborane-based rotors*

First, let us consider friction at the molecular level. Our MD simulations show that in most cases the rotors initially oscillate around their equilibrium orientation. When driving forces are applied, the rotors need some time to respond. In fact, they struggle with these three phenomena:

(I) The rotation barrier  $E_B$ . It needs to be overcome for rotation to occur. This is an issue in the beginnings of the simulations when the rotor is stopped or randomly oscillating. If the barrier is large, strong forces may be needed to start the rotor. This is sometimes called static friction. We rather suggest the term “gription”. It is not a real friction of the rotor because the process is energy conservative. Going down the barrier rotor gains back any energy it lost on its way up. Most of our rotors have very low rotation barriers.

(II) Thermal fluctuations. Stochastic forces strike the rotors randomly and often bring them out of synchronicity or can stop the rotation entirely. Thermal fluctuations can also help to start the rotor or get it over a barrier. When the temperature equivalent of the rotation energy is above the temperature of the system, the thermal fluctuations will on average tend to slow the rotor down. It always acts against unidirectional rotation. In order to synchronously drive molecular rotors the driving torque must be able to compete the thermal motion.

(III) Dynamics friction. This is the real friction of molecular rotors. It creates a torque acting to slow the rotor down and constantly drains energy from the rotation mode. It is the result of thermal fluctuations in cases when the rotor energy is well above  $kT$ . If the rotor energy is below  $kT$  the rotor would quickly reach the equilibrium energy but it would only randomly oscillate.

Considering this we can identify the friction at the molecular level as the intermolecular vibration energy redistribution (IVR) in physical chemistry or as heat conductivity in thermodynamics. In this process the energy of the rotation mode is redistributed into vibration modes of the supporting substrate and the rotor itself, providing the rotational excitation is above equilibrium excitation of the other modes. Or, we can say the heat flows from one mode to a bath. From this it comes that the rate of energy dissipation should be proportional to the temperature difference between the rotational mode and the bath and hence the friction torque should be proportional to angular velocity in the high frequency limit:  $N = \eta(I\omega/2R - T^0/\omega)$ .

Thus we can expect the friction to be strongly system dependent and to increase with strength of coupling between the rotor and the mounting grid. Since we are dealing with molecules, the vibration modes manifold of the molecular grid will be important for the coupling.

We have used the methods described in our papers<sup>1,3</sup> to estimate friction in carborane molecular propellers. See attachment 1 for more details.

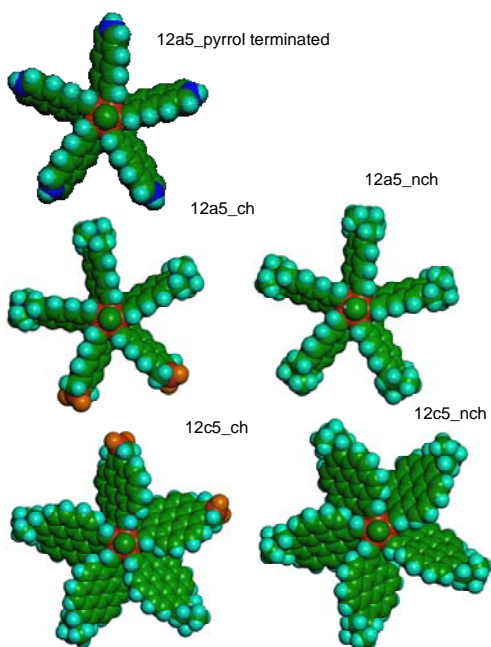


Fig. 1: 12 vertex carborane propellers

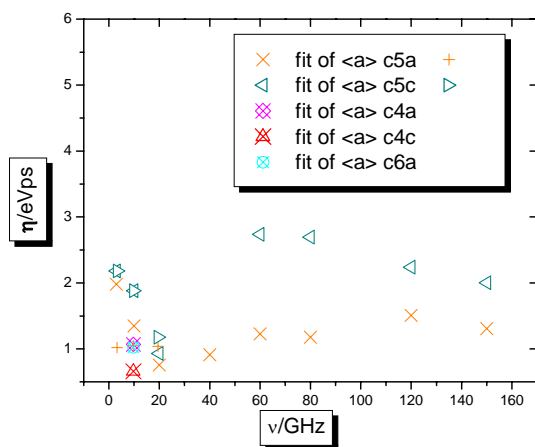


Fig.2: Molecular propeller friction coefficient on frequency (example)

## (2) Simple model of molecular propellers in gas flows

We finished our simple model of gas driven molecular propellers.<sup>3</sup> The model performs reasonably well. Fig. 3 compares examples of angular momentum evolution from MD and from the simple model. Currently, we are testing this model against a new group of porphyrin propellers. More details can be found in attachment 1.

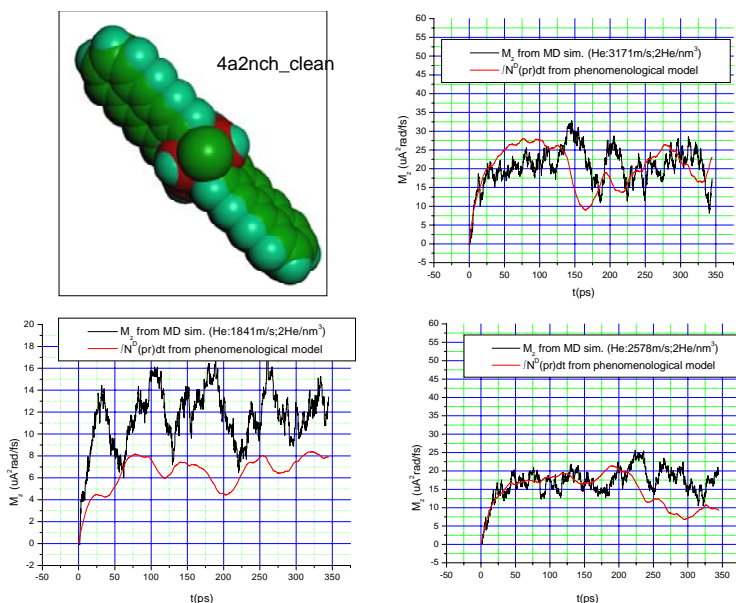


Fig. 3: Performance of gas drive simple model in predicting angular momentum

## (3) Second generation of the light-absorption driven molecular motor.

Based on our previously reported design<sup>2</sup> we tried to improve the structure and performance of our light-absorption driven molecular motor. We wanted to use sturdier motor stands and better electron donor/acceptor groups. The structure was mounted on a cubic zirconia surface in the computer and preliminary simulations performed (the stands were designed to adhere to cubic zirconia). Simulations in supercritical CO<sub>2</sub> are underway. We want to investigate the possibility to pump gases or liquids using this motor. Details will be published in reference 4.

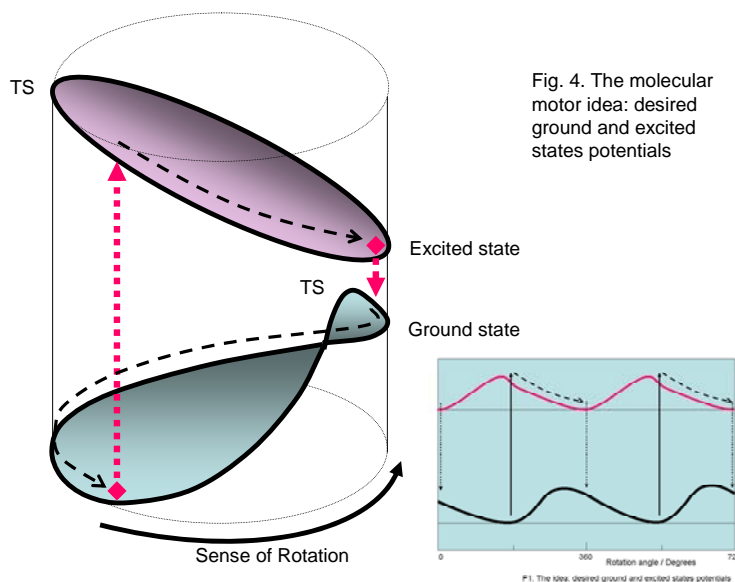


Fig. 4. The molecular motor idea: desired ground and excited states potentials

P.1. The idea, desired ground and excited states potentials

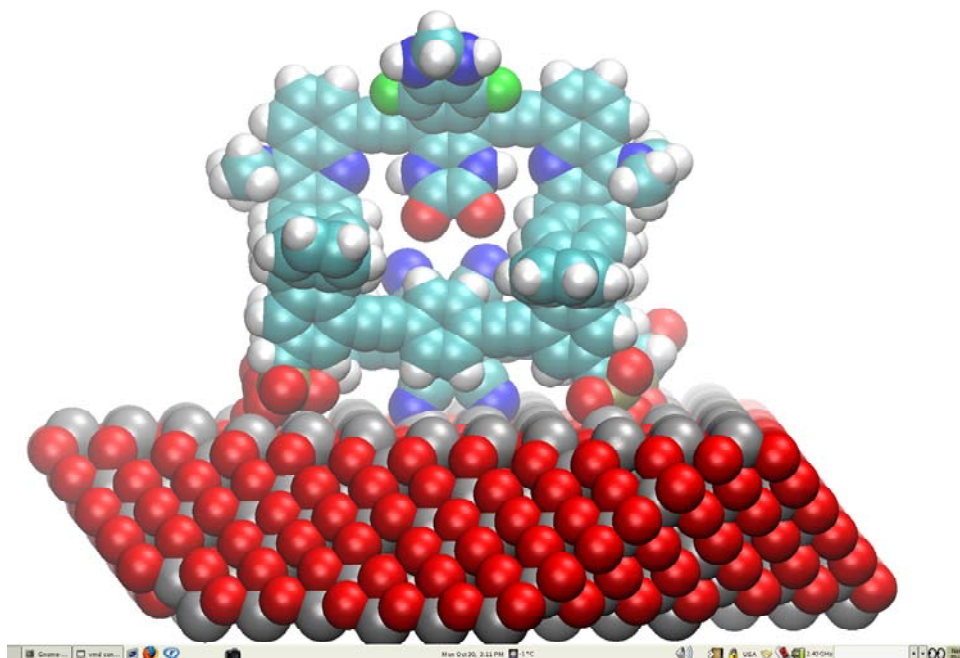


Fig. 5: New molecular motor on cubic zirconia

### Significance to DoD

Our simulations suggest that both passive (gas flow driven) molecular paddle wheels and propellers and active (light-absorption driven) molecular motors and paddle wheels can be used to modify and perhaps control friction of surfaces. We studied only several particular designs and lot is yet to be investigated. Molecular motors and switches can also be useful in optics, electronics and molecular electronics.

### Travel and Presentation of Results

Vacek, J., Chocholoušová, J., Kobr, L., Miller, J., and Michl, J. Proceedings of the HPCMP Users Group Conference, DoD High Performance Computing Modernization Program, IEEE, 2006.<sup>2</sup>

Two more papers to be submitted.<sup>3,4</sup>

### Conclusions

- Friction of carborane-based turbines was evaluated using several different methods.
- Second generation of a light-absorption motor has been designed.
- Simple gas-drive models were prepared.
- We conclude that both passive and active molecular rotors (motors) are feasible, can rotate in gas flows, in electric fields, and may be useful in designing new materials and surfaces.

### References

- 1 Vacek, J.; Michl, J. *PNAS* **2001**, 98, 5481.
- 2 Vacek, J., Chocholoušová, J., Kobr, L., Miller, J., and Michl, J. Proceedings of the HPCMP Users Group Conference, DoD High Performance Computing Modernization Program, IEEE, 2006.
- 3 Prokop, A., Vacek, J., Michl, J., „Friction in molecular propellers“, *J. Am. Chem. Soc.*, to be submitted.
- 4 Vacek, J., Kobr, L., Miller, J., and Michl, “Design and Molecular Dynamics Simulation of a Fast Artificial Light-Absorption Driven Molecular Rotor”, to be submitted.

### Attachments

- 1 Copy of our friction paper draft.<sup>3</sup>
- 2 Movie of the molecular motor action.
- 3 Invoice for 0004.